FABRICATION AND CHARACTERIZATION OF SOME POLYMER-NANO METAL OXIDE COMPOSITES FOR PHOTOCATALYSIS AND RELATED APPLICATIONS

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The thesis entitled ‘‘**Fabrication and characterization of some polymer-nano metal oxide composites for photocatalysis and related applications**’’ focusses on fabrication, characterization, and photocatalytic applications of polymer (zein, hydroxyethyl cellulose, chitosan, and polyaniline)/metal oxide (CuO, TiO_2, and ZnO) composites. The work covers five chapters.

Chapter 1: **Overview of advancements on polymer/metal oxide hybrid nanocomposite photocatalyst and catalysis**

Chapter 2: **Enhancing the recyclability of polyaniline/TiO_2 hybrid nanocomposite by immobilizing with zein/ hydroxyethyl cellulose functionalized composites for removal of anionic dyes**

Chapter 3: **Polyaniline grafted CuO/ZnO photocatalyst for the removal of anionic and cationic dyes**

Chapter 4: **Chitosan/hydroxyethyl cellulose gel immobilized polyaniline/CuO/ZnO adsorptive-photocatalytic hybrid nanocomposite for anionic dye removal**

Chapter 5: **Improving photocatalytic and antibacterial properties of zein/polyvinyl alcohol polymer composite film by dispersing TiO_2 nanoparticles**

CHAPTER 1

Overview of advancements on polymer/metal oxide hybrid nanocomposite photocatalyst and catalysis

1.1 Introduction

Photocatalysis is a process where light and catalysts are at the same time speeding up a chemical reaction. When light is induced to the reaction system, activation energy is lowered, and thus the reaction rate is enhanced as compared without light. After the reaction has been completed, the catalyst is generated with its characteristic properties [1]. Catalysts in industries play an imperative role in economic development and environmental remediation. In chemical industries, more than 75% of the chemicals are produced with the help of catalysts. Advancements in the newly developed process showed catalyst-supported products are crossing 90%. Plastics, synthetic fibers, medicines, crop-protection agents, resins, dyes, and pigments cannot be produced without the use of a catalyst [2]. Their mode of implementation is either identical (homogeneous) to the substrate phase or different (heterogeneous). Hence, depending on the nature of the catalyst, the catalysis is either homogeneous or heterogeneous.

1.2 Classification photocatalysis

The catalysis process can occur in single (homogenous) or different (heterogeneous) phases based on the catalyst and reactant phases.

1.2.1 Homogeneous photocatalysis

All the species in the homogeneous photocatalysis reaction path are in a single phase (solution). Due to stability and electronic bandgap, transition metal complexes like iron, copper, chromium, etc., are commonly used for the homogenous catalysis process. In such a catalytic process, under the photon and thermal conditions, the higher oxidation state of metal ion complexes generates hydroxyl radicals. Then, these hydroxyl radicals react with organic matter, which leads to the destruction of toxic matter. Ozonation and Fenton process (Fe (II) salt and H_2O_2) are frequently

practiced in the homogeneous photocatalytic processes. Because of the ease of operation, non-toxicity, high performance of oxidation, it requires ambient temperature and pressure [3, 4].

$$Fe^{2+} + H_2O_2 \rightarrow HO^{\cdot} + Fe^{3+} + HO^{-} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow HO_2^{\cdot} + Fe^{2+} + H^{+} \quad (2)$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^{-} \quad (3)$$

The Photo Fenton technique is advantageous in harvesting sunlight at longer wavelengths (up to 450 nm) and thus eliminates high-cost UV light and energy consumption. Despite being more efficient than others, it only works at lower pH because higher pH causes iron to precipitate, and removing iron after catalysis at lower pH is also challenging.

Exposing the ozone molecule to light ($\leq$330 nm) leads to its breakdown into oxygen molecule and atom. Further interaction of oxygen atom with water produces active species free hydroxyl radical and hydrogen peroxide, which is used for destroying hazardous chemicals and microbial species [5].

$$O_3 + hv \rightarrow O_2 + O^{\cdot} \quad (4)$$

$$O^{\cdot} + H_2O \rightarrow 2HO^{\cdot} \quad (5)$$

$$O^{\cdot} + H_2O \rightarrow H_2O_2 \quad (6)$$

$$H_2O_2 + hv \rightarrow 2HO^{\cdot} \quad (7)$$

1.2.2 Heterogeneous photocatalysis

In heterogeneous photocatalysis, the catalyst (photosensitizer) and the reactant are in different phases. Transition metal oxides and semiconductors have been investigated as heterogeneous photocatalysts. Semiconductors are the most commonly used for various applications [6]. The general mechanisms in heterogeneous catalysis involve light absorption, electron excitation, active species (free radicals, superoxide, etc.) formation, and degradation. In the first step, light energy equivalent or greater than binding energy is absorbed on the surface of the catalyst, causing electron excitation from valence band (higher occupied orbital) (VB) to conduction band (lower unoccupied orbital) (CB). This leads to the production of positively charged holes in the VB and negatively charged electrons on the CB, as shown in fig. 1. These holes react with electron-donating species to generate strong oxidizing species. Likewise, the electrons in the CB react with

surface adsorbed oxygen molecules to form a superoxide anion. Both species produced in VB and CB cause degradation (mineralization) of toxic species such as organic pollutants, microbial species, etc. [7].

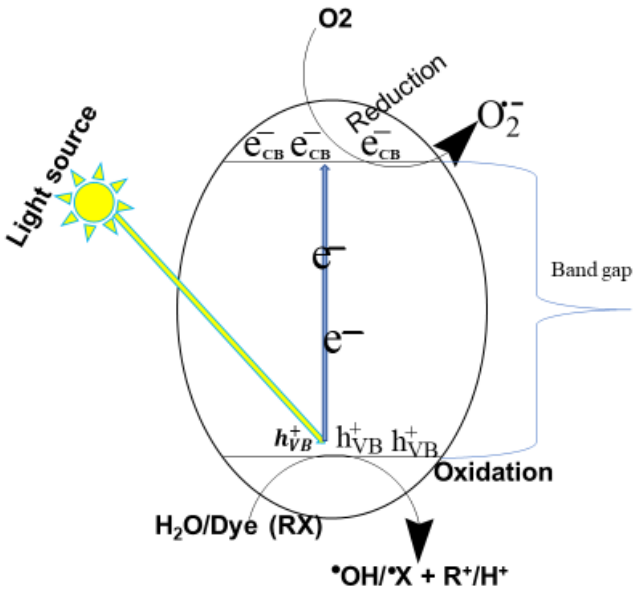

Fig.1.1 Photocatalytic mechanisms by heterogeneous photo(electro) catalyst

Compared with homogeneous photocatalysis, heterogeneous photocatalysis is technically better to implement in industrial processes, due to improved stability, ease of recoverability, and recyclability of the heterogeneous catalysts [4]. Among heterogeneous catalysis, metal oxide-based photocatalysts were most investigated for various catalysis application properties due to ease of fabrication with unique surface morphology and tunable properties [8]. For example, metal oxide nanoparticle photocatalysts such as TiO_2 and ZnO are nontoxic, compatible, cheap, and capable of absorbing light energy [9]. They have high surface area, unique physicochemical properties, size-dependent optical and catalytic properties [10]. They can also be manufactured in a simple, practicable, low-cost, and environmentally friendly manner [9, 11– 13]. However, metal oxide nanoparticle photocatalysts are rapidly agglomerated, have a short shelf life, lose their surface activity, optical property, and efficiency [14]. In addition, it is difficult to achieve efficient light absorption in the visible region, effective photocatalytic activity, stable hole-electron separation, good stability, and facile recovery and recycling from a pristine metal oxide nanoparticle [15]. Studies showed that polymers and metal oxides could be employed together to increase visible light absorption capacity and reduce charge recombination, agglomeration,

recovery, and recyclability because polymer's optical, structural, and electrical properties are relatively managed and can develop at the molecular level.

Furthermore, polymers have a high surface area, multiple active sites, good mechanical strength, and stability [16]. Hence, hybridizing polymers with metal oxide nanoparticles induced synergetic optical, catalytic, mechanical, electrical, and other properties. Thus, it is due to polymers that polymer/metal oxide hybrid nanocomposite photocatalysts become stable, porous, have a long shelf life, a large surface area, are efficient, recyclable, and recoverable [17, 18]. From such points of view, the polymer/metal oxide hybrid composites cannot be compared to pure metal oxide nanoparticle photocatalysts because nearly all of the disadvantages of pure metal oxide nanoparticle photocatalysts are eliminated in polymer/metal oxide hybrid photocatalysts. As a result, incorporating polymers into metal oxide hybrid photocatalysts is vital since they allow for the production of recyclable and long-lasting photocatalysts [17, 19]. The cost-effectiveness of polymer/metal oxide hybrid photocatalysts is attributable to their recoverability, recyclability, and other synergistic properties. The cheap and environmentally friendly sources of biopolymer make the most preferred [20]. Based on such facts, this review addressed the basic concepts, fabrication techniques, and the current achievements of hybrid composite photocatalysts used for antibacterial and dye degradation applications. It gives special attention to polymer/metal oxide hybrid nanocomposite materials used in heterogeneous photocatalysis reactions. The degradation mechanism, kinetics, efficiency, and factors affecting the composite materials also have been assessed.

1.3 Fabrication technique adopted for polymer/metal oxide hybrid nanocomposite

The daily increment in the potential application of polymer/metal oxide hybrid nanocomposites accelerates various fabrication strategies. These fabrication strategies can be summarized into two major routes as *in-situ* and *ex-situ* (direct mixing or blending) processing techniques [21].

1.4 Mechanism of adsorptive assisted photocatalytic degradation

The degradation mechanism involves two sequential steps (adsorption followed by photocatalytic degradation) [22]. Since such catalysis is in a heterogeneous system, the phenomena are surface-

dependent. The nature of the hybrid surface determines the rate of an adsorptive-catalytic process [23]. The presence of active sites, functional groups, and a large surface area on the composite accelerate the adsorption of molecules to the surface of the catalyst, allowing accessible holes and electrons to easily interact with the molecules adsorbed on the surface, resulting in a rapid photocatalytic degradation reaction [24, 25].

In the overall mechanisms, hole-electron charge separation is generated by electron excitation from the valence band to the conduction band by absorbing photon energy greater than or equal to the bandgap energy [26]. After the positively charged hole and negatively charged electron have been created, the photocatalytic degradation mechanism occurs either directly or indirectly [27]. The positively charged holes directly interact with the substrate (organic matter) in a direct photocatalytic degradation mechanism, forming reactive radical species, which accelerates autoxidation of the substrate into degradation products. While in the indirect photocatalytic degradation reaction, the solvent and other dissolved species other than the substrate, such as water and oxygen molecules, combine with the charged holes and electrons to generate reactive species, which further interact with the substrate molecules. The solvent (usually water) is oxidized by the positively charged holes, producing radicals (hydroxyl radicals) and other species. The hydroxyl radicals further attack organic pollutants and undergo various chain reactions. The oxygen adsorbed on the conduction band is reduced by the excited electron forming superoxide anionic radicals ($O_2^{\cdot -}$). The oxygen superoxide radicals react with a proton to produce hydroperoxyl ($HO_2^{\cdot}$) and hydrogen peroxide (H_2O_2). These active species again react with organic pollutants to form degradation products like water, carbon dioxide, and other mineralized nontoxic products [28-30]. Both direct and indirect photocatalysis occur at the same time. However, the principal degradation path depends on the species' physicochemical interaction with the catalyst surface. Suppose the substrate's (pollutant's) interaction with the photocatalyst is more favorable than other species present in the reaction media. Then, the main catalytic degradation path follows direct photocatalysis, and the opposite is true for indirect photocatalysis [31].

When a polymer/metal oxide hybrid nanocomposite is exposed to light in the reaction media, the metal oxide nanoparticle, polymer, and occasionally the substrate can absorb photons at the interface and excite electrons based on their bandgap energy. Those species having lower bandgap energy are the major contributors to electron excitation. The remaining having higher bandgap

energy enhances degradation by preventing charge recombination since they trapped excited electrons to their conduction bands [32]. Hence, the synergistic effects of the polymers, substrates, and metal oxide nanoparticles accelerate light-assisted degradation reactions. Depending on the easy electron releasing species or bandgap energy difference, photocatalytic degradation reactions can be classified as polymer sensitized, metal oxide sensitized, and substrate(dye)-sensitized degradation reactions. All of the possible steps of sensitization mechanisms are explained. However, this review focused on details of polymer and metal oxide sensitized dye and bacterial degradation reaction by polymer/metal oxide hybrid composite as its target.

1.5 Photocatalytic degradation by polymer/metal oxide hybrid nanocomposite

As stated before, the dye degradation reaction by polymer/metal oxide hybrid nanocomposite is sensitized by either the polymer or the metal oxide nanoparticles, depending on their bandgap energy. Once the degradation reaction starts, it does not mean that it will undergo until completion. Other factors like surface area, porosity, functional groups, pH, temperature, nature of the hybrid composites, etc., affect the overall reaction [33]. Hence, associated factors should also be considered in the polymer/metal oxide hybrid nanocomposite catalytic degradation. The photocatalytic degradation by the polymer/metal oxide nanocomposite can be summarized as conductive polymer/metal oxide, non-conductive polymer/metal oxide, and mixed polymer (conductive and non-conductive)/metal oxide hybrid nanocomposites

1.6 Research Gap

Metal oxide-based photocatalysts were most investigated for various catalysis application properties due to ease of fabrication with unique surface morphology and tunable properties. They have high surface area, unique physicochemical properties, size-dependent optical and catalytic properties. Their manufacturing process is also simple, practicable, low-cost, and environmentally friendly. However, metal oxide nanoparticle photocatalysts are rapidly agglomerated, short shelf life, lose their surface activity, optical property, and efficiency. In addition, it is difficult to achieve efficient light absorption in the visible region, effective photocatalytic activity, stable hole-electron separation, good stability, and facile recovery and recycling from a pristine metal oxide nanoparticle. Various investigations showed that the role of polymers in polymer/metal oxide

hybrid composite is paramount to sensitize the catalytic reaction, enhance surface adsorption, prevent nanofiller aggregation, and increase stability and recyclability. Thus, the use of synthetic and natural polymers has proven to be effective in creating dual-functional (adsorptive and catalytic), recoverable, and recyclable polymer/metal oxide hybrid nanocomposite photocatalytic materials. Therefore, polymer/metal oxide hybrid nanocomposite will become a viable option for catalyzing light-driven catalytic reactions in the future. Hence, such a thematic area provides fresh insight for the researchers in developing environmentally safe synthetic and natural-based metal oxide hybrid nanocomposites for catalytic degradation of dyes, bacteria, and other related emerging organic pollutants. Based on such facts, the following general and specific objectives were anticipated.

1.6.1 General objective

To manufacture some polymer/nano metal oxide composite for photocatalytic degradation of organic pollutants and bacteria

1.6.2 Specific objectives

- To synthesize and characterize
  - ✓ Zein/hydroxyethyl cellulose/polyamine/TiO_2 functionalized composite
  - ✓ Poly aniline/nano-CuO/ZnO composite
  - ✓ Chitosan/HEC gel immobilized poly aniline/nano-CuO/ZnO composite
  - ✓ Zein/polyvinyl alcohol/TiO_2 antibacterial composite film
- To evaluate the catalytic activity of the catalyst for degrading model organic pollutants and bacterial species

CHAPTER 2

Enhancing the recyclability of polyaniline/TiO_2 hybrid nanocomposite by immobilizing with zein/HEC functionalized composites for removal of anionic dyes

2.1 Introduction

TiO_2 nanoparticle is selected as a photocatalytic agent in the current study due to the chemical stability, non-toxicity, compatibility, and conductivity [13]. However, it was reported that the aggregation of nanoparticles and recombination of excited electrons due to strong coulombic interaction strongly affect its catalytic activity during the reaction [14, 34]. Hybridizing it with conductive polymers could reduce the instability of charge separation between the valence and conduction band and the aggregation of nanoparticles [35]. Polyaniline is the one that was exclusively used to boost the photocatalytic function of TiO_2 due to its low bandgap energy and ability to excite electrons by absorbing light energy. Thus, TiO_2 nanoparticles in the hybrid composite trapped excited electrons to its conduction band, and hence the catalytic reaction is enhanced due to electron-hole stabilization [36]. However, it is not easy to recover the slurry of polyaniline/TiO_2 from the final product, particularly in large-scale treatment [37, 38].

Furthermore, these suspensions from the reaction medium prevent the incoming light from penetrating the entire part of the reaction system [39]. This effect limits the performance capacity of the photocatalyst in addition to the challenge of separation. Accordingly, it is vital to enhance the photocatalytic efficiency and recyclability of the polyaniline/TiO_2 (PANI/TiO_2) photocatalyst. Thus, the study deals with enhancing and immobilizing this photocatalyst with a zein/hydroxyethyl cellulose (zein/HEC) anchoring agent.

Zein comprises prolamine containing more than 50% hydrophobic residues of amino acids. Its hydrophilic nature could be enhanced by blending with water-soluble polymers due to hydrogen bonding between constituent species [40]. Composites of zein with hydrophilic polymer also possess a rough structure with high surface area microholes due to the self-aggregation of hydrophobic amide groups favored by hydrophilic group repulsion [41]. In addition, a large number of active groups disclosed and positively charged functionalized networked porous

structures of zein formed in acidic conditions [42, 43]. The microholes, functionalized porous structures, and different groups in the composite produce synergetic properties towards water absorption [40, 44]. This property is essential to support the adsorption of water-soluble pollutants to the heterogeneous catalyst surface. Furthermore, the strong interaction between zein and polyaniline makes the immobilization of the photocatalyst effective [45].

Hydroxyethyl cellulose is a well-known stabilizer, binder, and water retainer in various composite products due to its high viscosity and stability in all pH ranges [46]. Hence, zein and Hydroxyethyl cellulose composites are suggested to be stable and water-absorbing. Based on these facts, blending PANI/TiO_2 with zein/HEC composite immobilizes and increases adsorptive-assisted catalytic function due to the combined effects of factionalized structures and various active groups.

2.2 Methods

The zein/HEC/PANI/TiO_2 hybrid nanocomposite was produced by *in-situ* oxidative polymerization followed by immobilization via ex-situ dispersion and functionalization of an adhesive agent. The synthesized zein/HEC/PANI/TiO_2 photocatalyst was characterized by field emission scanning electron microscope (FESEM), energy dispersive X-ray (EDX), thermogravimetric analysis (TGA), powder X-ray diffractometer (XRD), and Fourier transform infrared spectroscopy (FTIR) instruments. The composite photocatalytic degradation efficiency was optimized based on TiO_2 proportion, catalyst dosage, and pH. The reflux titrimetric standard method designed by the UK environmental agency was applied for dye degradation COD analysis. A similar COD determination approach is also applied in chapters 3 and 4. Recoverability and reusability metrics were used to assess the economic viability of the catalyst.

2.3 Results

An acidic solution containing green PANI/TiO_2 activated different amide groups of the zein, and thus photocatalytic degradation of methyl orange is enhanced. More than 97.9% of methyl orange undergoes decolorization within 110 minutes. Even the performance of zein/HEC/PANI/TiO_2 photocatalyst was 94% after five cycles, indicating its high stability and recyclability. The kinetics of the reaction followed the first-order reaction. The COD decrease after photocatalytic treatment is due to methyl orange mineralization into water, carbon dioxide and other mineralized product.

In summary, the newly synthesized photocatalyst is an invaluable alternative for removing dyes (especially anionic dyes) from wastewater.

CHAPTER 3

Polyaniline (PANI) grafted CuO/ZnO photocatalyst for the removal of anionic and cationic dyes

3.1 Introduction

Various dye treatment methods based on chemical, physical, and biological approaches have been established [47]. The production of secondary pollutants, the complexity of methods, the high cost, low stability, and efficiency limit the use of many of these methods on a large scale [48]. At present, among other alternative approaches, polymer/metal oxide-based photocatalytic waste removal has become preferable due to its low cost, simplicity, and benign degradation product [49]. In this context, our research focuses on the synthesis, characterization, and use of polyaniline grafted CuO/ZnO photocatalyst for dye degradation removal. The PANI enhances substrate adsorption, prevents nanoparticle particle aggregation, increases mechanical strength and the surface area of the metal oxides in hybrid nanocomposites. At the same time, the CuO/ZnO is responsible for photocatalytic dye degradation. As a result, such a hybrid nanocomposite synergistically enhances photocatalytic degradation reactions [50, 51].

3.2 Methods

The PANI/CuO/ZnO composites were prepared by coprecipitation of CuO/ZnO followed by *in-situ* oxidative chemical polymerization of aniline. Then PANI/CuO/ZnO ternary composite was characterized by FTIR, FESEM-EDX, XRD, and TGA. In addition, **t**he effect of parameters like CuO/ZnO on PANI/CuO/ZnO composite, catalyst dosage, efficacy, and kinetic was investigated.

3.3 Results

The shift in FTIR characteristic peaks and decrease in fiber length of PANI from FESEM image in PANI/CuO/ZnO proved that PANI was effectively grafted in CuO/ZnO to produce PANI/CuO/ZnO composite. The XRD peak intensities of ZnO in CuO/ZnO were slightly reduced

due to ZnO partially embedded by CuO, and the EDX peaks of Cu and Zn in PANI/CuO/ZnO evidenced the presence of CuO/ZnO in the composite. This composite has better catalytic activity at 20% CuO/ZnO and is thermally stable than pure PANI. The photocatalytic degradation of crystal violet (CV) and methyl orange (MO) dyes followed first-order reaction kinetics with rate constant 0.00541 and 0.0415 $min^{-1,}$ respectively. Both crystal violet and methyl orange COD values were significantly decreasing, proving that there was mineralization of both dye molecules. The catalyst produced has enhanced photocatalytic degradation towards MO than CV due to the presence of a preferred force of attraction between the positively charged catalyst surface and negatively charged MO molecules.

CHAPTER 4

Chitosan/hydroxyethyl cellulose gel immobilized PANI/CuO/ZnO adsorptive-photocatalytic hybrid nanocomposite for anionic dye removal

4.1 Introduction

Incorporating multifunctional polymeric materials into inorganic nanoparticles results in a synergistic improvement in surface area, mechanical strength, adsorption capacity, recyclability, and photocatalyst's catalytic efficiency attract researchers to develop novel catalytic materials [51, 52]. With these regards, this study deals with developing stable, efficient, recyclable, and easily recoverable chitosan/hydroxyethyl cellulose (CS/HEC) gel immobilized polyaniline/CuO/ZnO (PANI/CuO/ZnO) hybrid nanocomposite photocatalyst for removing dye molecules from an aqueous environment.

4.2 Method

The CS/HEC gel immobilized PANI/CuO/ZnO nanocomposite photocatalyst was produced by *in-situ* oxidative polymerization of aniline containing CuO/ZnO followed by *ex-situ* dispersion of PANI/CuO/ZnO to CS/HEC gel matrix. The PANI/CuO/ZnO dispersed over less viscous HEC and glutaraldehyde solution followed by mixing with CS to effectively disperse and immobilize PANI/CuO/ZnO hybrid nanoparticles in the gel. The FESEM, FTIR, EDX, and TGA were used to characterize the hybrid composite. The effect of pH, PANI/CuO/ZnO, catalyst dosage, and

recyclability towards the degradation of Congo red efficiency was also assessed. In addition, the kinetics and degradation mechanisms were proposed using kinetics models and scavengers, respectively.

4.3 Results

According to UV-vis results, PANI/CuO/ZnO absorbance was observed in the longer wavelength than CuO/ZnO, showing that the bandgap energy of CS/HEC gel immobilized PANI/CuO/ZnO or PANI/CuO/ZnO is reduced due to hybridization of CuO/ZnO with PANI. The catalyst has higher degradation efficiency from neutral to lower acidic pH region. Even though degradation efficiency of CS/HEC gel immobilized PANI/CuO/ZnO photocatalyst increases with increasing PANI/CuO/ZnO, dispersion of PANI/CuO/ZnO to CS/HEC gel was limited to 60% due to the decrease in gel formation of the immobilizer. Based on the Langmuir-Hinshelwood model, the degradation of anionic dye (Congo red) (CR) followed a first-order reaction with correlation coefficients of 0.977 and it is 99.85% efficient in degrading congo red. The rapid decline of COD with irradiation time proved that Congo red was mineralized into CO_2, H_2O and other products. Generally, the catalyst produced is efficient, easily recoverable, and recyclable.

CHAPTER 5

Improving photocatalytic and antibacterial properties of zein/polyvinyl alcohol composite film by dispersing TiO_2 nanoparticles

5.1 Introduction

Plastics manufactured with fossil fuel emit toxic gases that pollute the ecosystem [53]. The gradual release of poisonous chemicals from petroleum-based plastic to the packed material cause health problem [54]. Besides, pure plastic packing materials produced from fossil fuel products are not efficient in preventing surface infections of packaged foods by harmful bacteria, fungi, and other microorganisms. To fight such problem, using environmentally friendly and compatible polymer composites by doping semiconductor metal oxide nanoparticles for packing and other application become a potential advantage [55, 56]. It provides safety and enhances packed materials' shelf life because doped polymer composites are more active than the bulk material in deactivating or

demolishing microorganisms [57]. Incorporating semiconductor metal oxide nanofillers into the polymers also increases composite film stability [58]. Therefore, improving photocatalytic and antibacterial activities of biopolymer-based composite by metal dioxide nanoparticles is vital for developing environmentally safe polymer hybrid composite. Hence, this chapter is aimed to investigate the feasibility of synthesizing, characterizing, and testing the catalytic and antibacterial activities of zein/PVA/nano-TiO_2 composite film crosslinked by glutaraldehyde.

5.2 Methods

The zein/PVA/nano-TiO_2 composite film was fabricated by *ex-situ* dispersion of TiO_2 followed by solution casting. The water absorption capacity, tensile strength, breaking elongation, morphological, thermal, and chemical properties were examined. The Chung-Pfost, Halsey, Oswin, and Henderson models were used to describe the effect of environmental humidity on moisture absorption of the composite film. The FESEM, TGA, and FTIR were used for morphological, thermal, and functional group-related properties. Batch catalytic reactor and disk diffusion method were used to study light-assisted catalytic degradation of methyl orange dyes and gram-negative and positive bacterial species.

5.3 Results

The water absorption properties and surface smoothness of zein/PVA/TiO_2 increase with PVA proportion. But films having low water absorption capacity are recommended for packing material. Hence, zein to PVA proportion with 5/3 has low water absorption capacity. Hence based on this proportion, tensile strength, breaking elongation, equilibrium moisture content, and other properties were studied. The maximum tensile strength and breaking elongation were achieved at 0.4% TiO_2 in the composite. Even though tensile strength varies with TiO_2 proportion, the R^2 value in the 5% confidence level showed no remarkable changes. The characteristics bands of FTIR at 515 cm^{-1} and XRD peaks at different positions and uniform morphology of SEM image showed that effective dispersion of TiO_2 nanoparticles. Insignificant weight changes up to 200 ^oC indicated the composite films' thermal stability. The film can degrade both organic pollutants and bacteria. More than 85% methyl orange degraded within half an hour. The composite also has antibacterial activity with a zone of inhibition of 27.57 mm and 25.73 for gram-positive *S. aureus* and gram-

negative *E. col*, respectively. The overall result proved that the developed film could be a possible alternative for producing surface protective packaging materials and other photocatalytic-related application

6. The Overall outcome of the study

In-situ oxidative polymerization and *ex-situ* dispersion were commonly used to synthesize polymer-metal oxide-based hybrid nanocomposites. PANI/TiO_2 and PANI/CuO/ZnO hybrid nanocomposites were efficiently produced by in-situ oxidative polymerization after dispersing TiO_2 and CuO/ZnO nanoparticles in aniline solution. The PANI/TiO_2, PANI/CuO/ZnO hybrid nanocomposites, and TiO_2 nanoparticles were successfully immobilized by glutaraldehyde crosslinked zein/HEC, zein/CS and zein/PVA composites via ex-situ dispersion, respectively. As a result, these composites are efficient, recoverable, and recyclable for UV-visible light catalytic dye degradations. Most of the dye molecules were mineralized to CO_2, water and other not toxic products. In addition, the zein/PVA/TiO_2 composite film was tested for UV catalytic antibacterial action, and both gram-negative and positive bacterial growth were inhibited. Hence, the use of synthetic polymers and natural polymers have proven to be effective in producing dual-functional (adsorptive and catalytic), recoverable, and recyclable polymer/metal oxide hybrid nanocomposite capable of converting dyes and related emerging pollutants into mineralized products. And thus, polymer/metal oxide hybrid nanocomposite becomes a viable option for catalyzing light-driven adsorptive assisted catalytic reactions and producing surface protective packaging materials.

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List of publications

1. **Tadesse Bassie Gelaw**, Balladka Kunhana Sarojini, Arun Krishna Kodoth ''Review of the Advancements on Polymer/Metal Oxide Hybrid Nanocomposite-Based Adsorption Assisted Photocatalytic Materials for Dye Removal,'' *ChemistrySelect: Chemistry Europe(Catalysis), 6*, 9300 –9310, 2021, doi.org/10.1002/slct.202102020
2. **Tadesse Bassie Gelaw,** Balladka Kunhana Sarojini**, ''**Enhancing the Performance and Recyclability of Polyaniline/TiO_2 Hybrid Nanocomposite by Immobilizing with Zein/Hydroxyethyl Cellulose Composites for Removal of Anionic Dyes,'' *Asian Journal of Chemistry*, 33, 1253-1260, 2021, doi.org/10.14233/ajchem.2021.23169
3. **Tadesse Bassie Gelaw,** Balladka Kunhana Sarojini, Arun Krishna Kodoth**, ''**Chitosan/Hydroxyethyl Cellulose Gel Immobilized Polyaniline/CuO/ZnO Adsorptive-

Photocatalytic Hybrid Nanocomposite for Congo Red Removal,'' Journal of Polymers and the Environment, 30, 4086–410, 2022. https://doi.org/10.1007/s10924-022-02492-4

4. **Tadesse Bassie Gelaw**, Balladka Kunhana Sarojini, ''Improving Photo Catalytic and Antibacterial Properties of Zein/Polyvinyl Alcohol Polymer Composite Film by Dispersing TiO_2 Nano Particles,'' Journal of Polymer & Composites, 8, 110-127,2020. doi.org/10.37591/jopc. v8i2.4258
5. Tadesse Bassie Gelaw, Balladka Kunhanna Sarojini, ''Enhancing the Performance and Recyclability of Polyaniline/TiO_2 Hybrid Nanocomposite by Immobilizing with Zein/Hydroxyethyl cellulose Composites for Removal of Anionic dyes'', Research square, https://doi.org/10.21203/rs.3.rs-207633/v1

List of papers presented in an international Conferences

6. **Tadesse Bassie Gelaw**, Balladka Kunhana Sarojini, ''Polyaniline grafted CuO/ZnO photocatalyst for the removal of anionic and cationic dyes,'' International Online Conference on **Materials Science and Technology** (ICMT 2021) 12th -14th November 2021,Mahatma Gandhi University, Kottayam, Kerala, India
7. **Tadesse Bassie Gelaw**, Balladka Kunhana Sarojini, ''Enhancing the Performance and Recyclability of Polyaniline/TiO_2 Hybrid Nanocomposite by Immobilizing with Zein/Hydroxyethyl Cellulose Composites for Removal of Anionic Dyes, International Conference on **Water : From Pollution to Purification**, December 12-14 (ICW 2020), Inter University Instrumentation Centre (IUIC) and School of Environmental Sciences, Advanced Centre of Environmental Studies and Sustainable Development (ACESSD), Mahatma Gandhi University, Kottayam, Kerala, India

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